Tutor/s

Dra. Rosa Albalat Piñol
Departament de Ciència de Materials i Química Física

Dr. Carlos Rodríguez Abreu
Institut de Química Avançada de Catalunya (IQAC-CSIC)

Grau de Química

Treball Final de Grau

Chromonic líquid crystals as precursors of polymer nanofibers

Cristalls líquids cromònics com a precursors de nanofibres de polímers.

Santiago Pons Allés

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Universitat de Barcelona

B:KC Barcelona Knowledge Campus
Campus d'Excel·lència Internacional

Investigar es ver lo que todo el mundo ha visto, y pensar lo que nadie más ha pensado.

Albert Szent

En primer lloc m'agradaria donar les gràcies al Dr. Carlos Rodríguez Abreu per la seva gran ajuda i orientació per elaborar aquest treball durant tots aquests mesos.

Agrair a tots els companys del grup de Química Col·loïdal i Interfacial, per acollir-me tant bé i resoldre els mil i un dubtes que sorgeixen en moure's en un nou entorn amb una paciència infinita.

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REPORT

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1. SUMMARY

Chromonic liquid crystals (CLCs) are a special kind of the well-known lyotropic liquid crystals. These mesophases are formed by multi-ring aromatic molecules like dyes, drugs or nucleic acids; which in the appropiate concentrations tend to aggregate forming columns. They have special properties that make them very interesting, including tailored optical properties.

In this work, four different dyes (3,3'-Diethylthiadicarbocyanine iodide; 3,3'-Diethylthiacarbocyanine iodide; Pinacyanol chloride and Neutral Red) have been studied regarding their capacity for liquid crystal phase formation and their use as templates for oriented polymer nanofibers, some encouraging results were obtained.

The synthesis strategy is based on a counterion exchange with a polymerizable ion (acrylate), followed by self-assembly to obtain an homogeneous nematic phase which is used as medium for free-radical polymerization. Since in CLCs counterions are located in the periphery of the molecules, polymerization takes place in the surface of the columns of the dye's nematic phase as template, so that polymeric nanofibers are obtained.

Different techniques have been used for the characterization of the produced materials, such as IR spectroscopy, Small Angle X-ray Scattering (SAXS) and SEM imaging. The best results were those obtained using Pinacyanol acrylate as precursor, nanofibers of about 100-400 nm of thickness and a few microns length were synthetized.

The polymeric nanofibers obtained are very suitable for further studies involving development of new optical polarizers, innovative higher performance solar cells and membranes. Moreover, the optical properties can be tuned depending on the precursor used, implying a very wide range of different possible applications making CLCs a very attractive field of study.

Keywords: Chromonic liquid crystals, lyotropic liquid crystals, nanofibers, template polymerization, polarization

2. RESUM

Els cristalls líquids cromònics (CLCs) són un tipus especial dels coneguts com cristalls líquids liotròpics. Aquestes mesofases estan formades per molècules aromàtiques de més d'un anell com ara fàrmacs, colorants o àcids nucleics. Tenen propietats especials que les fan molt interesants, com ara propietats òptiques fetes a mida.

En aquest treball s'han estudiat quatre colorants diferents (3,3'-Diethylthiadicarbocyanine iodide; 3,3'-Diethylthiacarbocyanine iodide; Pinacyanol chloride i Neutral Red) gràcies a la seva capacitat per formar cristalls líquids i la seva utilitat com a plantilla per sintetitzar nanofibres polimèriques orientades, obtenint alguns resultats destacables.

L'estratègia de síntesi es basa en un intercanvi de contraió amb un ió polimeritzable (acrilat), seguit d'un procés d'autoensamblatge per obtenir una fase nemàtica homogènia que s'utilitzarà com a medi per una polimerització per radicals lliures. Com que en els CLCs els contraions es localitzen en la perifèria de les molècules, la polimerització tindrà lloc en la superfície de les columnes de la fase nemàtica del colorant com a plantilla, obtenint així nanofibres polimèriques.

S'han fet servir diferents tècniques per caracteritzar els materials obtinguts, com ara espectroscòpia IR, Small Angle X-Ray Scattering (SAXS) i microscòpia electrònica (SEM). Els millors resultats són aquells obtinguts utilitzant Pinacyanol Acrylate com a precursor, donant lloc a nanofibres d'entre 100 i 400 nm de gruix i unes quantes micres de llargada.

Aquest tipus de fibres podrien ser interessants en futurs estudis per desenvolupar nous polaritzadors òptics, cèl·lules fotovoltaiques innovadores de major rendiment i membranes. És més, les seves propietats òptiques poden ser ajustades depenent del precursor, això implica una ampla varietat de diferents aplicacions possibles, pel que els CLCs són avui en dia un camp d'estudi molt atractiu.

Paraules clau: Cristalls líquids cromònics, cristalls líquids liotròpics, nanofibres, polimerització amb plantilla, polarització

3. INTRODUCTION

3.1. LIQUID CRYSTALS

At first, the concept of liquid crystal (LC) may seem conflicting, as it implies two opposed terms: crystal and liquid. However, this notation is fully justified, since liquid crystalline phases present properties of a liquid like fluidity; but they also show properties of a crystalline phase, like spatial arrangement in one or more directions or anisotropy of some of its properties (optical, electric and magnetic properties).[1,2]

Liquid crystals phases are often referred to as mesophases, which indicates "between phases" as it could be considered as an intermediate state of matter, between liquid and crystalline phases.[1]

3.1.1. LCs classification

LCs can be divided in two general groups: lyotropic and thermotropic LCs. The main difference is that thermotropic LCs may show a phase transition with temperature variation; while lyotropic LCs show phase transitions as a function of two properties, temperature and concentration, being the concentration dependence what makes them more interesting.[3]

In addition, thermotropic LCs are not solvent dependent, while lyotropic LCs need a solvent to be able to form an organized crystalline structure.[3]

3.2. LYOTROPIC LIQUID CRYSTALS

Lyotropic liquid crystals have been a matter of interest since they display unique properties that their thermotropic cousins do not show. The main focus on the research on this kind of LCs has been on amphiphilic molecules and surfactants, however, there are other classes of LCs, like chromonic liquid crystals.[4]

3.2.1. Amphiphilic Liquid Crystals

Amphiphiles are molecules typically formed by a hydrophobic alkyl chain, attached to a hydrophilic head group. As the concentration of this molecules increases reaching the critical micelle concentration (CMC), they aggregate into micelles (Fig.1).

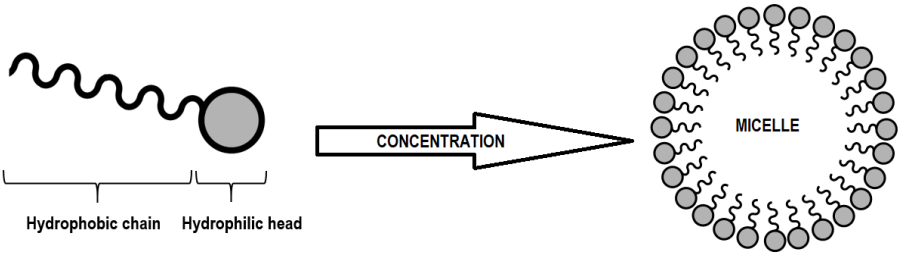


Figure 1. Schematic representation of micelle formation

If the concentration is increased even further, the formation of a whole host of liquid crystalline phases may be observed (Fig.2).[4,5]

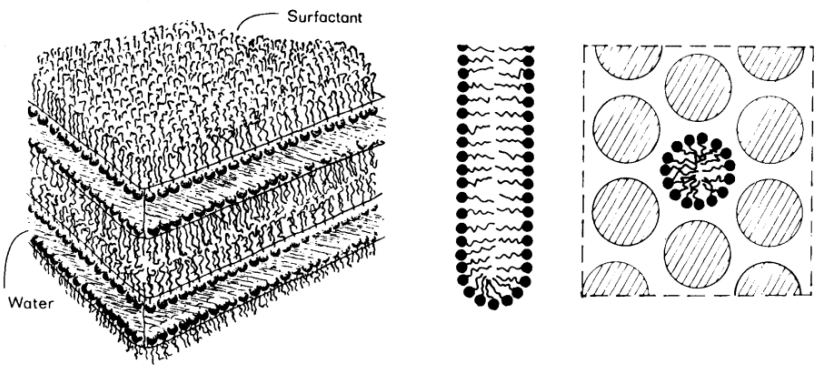


Figure 2. Lamellar phase (left) and hexagonal phase (right).
(Extracted from ref 6)

3.2.2. Chromonic Liquid Crystals

Chromonic liquid crystals (CLC) are a special kind of lyotropic mesophases, formed by soluble multi-ring aromatic compounds, these molecules could be considered like rigid aromatic planks, that aggregate forming stacks or columns (Fig.3). The solubilizing groups are usually on the periphery of the molecules, in the majority of the cases this solubilizing groups are ionic.[4,7]

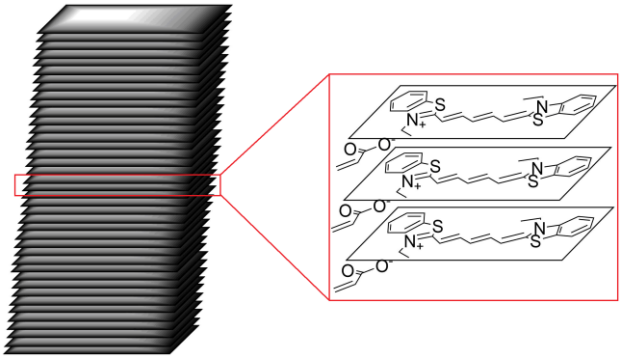


Figure 3. Representation of the column stacking of a thiacyanine-based dye

Chromonic phases are common in drugs, dyes, nucleic acids and any kind of molecule with the aromatic structure mentioned before.

There are different properties that make these mesophases special. First of all, there is no chromonic analogue of the critical micelle concentration mentioned before, that means that there is aggregation of the molecules in very dilute concentrations. It's also remarkable that the driving force doesn't seem to be entropic (like in micelle formation for amphiphilic molecules) since measurements of thermodynamic properties suggest that is enthalpic, caused by the interaction between π-orbitals of adjacent molecules.[7]

There are two classic chromonic mesophases, the nematic (N) phase, formed at lower concentrations and the hexagonal (M) phase, formed at higher concentrations (Fig.4).

In the N phase, molecules stacked in columns (as stated before) lie in a nematic array with no positional ordering, they are only aligned along a preferred direction on their long axes, being able to rotate on it.

In the M phase, molecules are also stacked in columns, but forming a hexagonal lattice.[7]

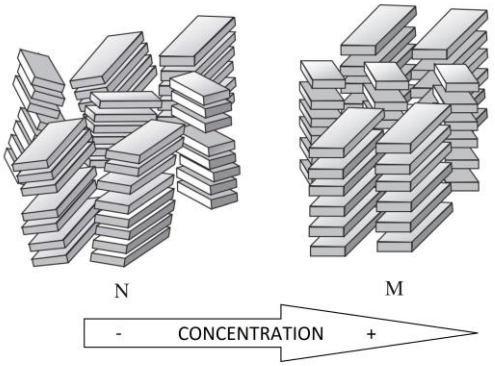


Figure 4. Nematic (N) and Hexagonal (M) phases
(Image adapted from ref 7)

There are also cases where the gradual change from N phase no M phase is not a clear borderline, so it exists an intermediate phase called P, where both N and M phases are present.[7]

It has been found that in some cases molecules stack forming hollow pipes (Fig.5), such as in the case of dyes CI Acid Red 266 and pseudo isocyanines[4].

In other cyanine dyes a "brickwork" structure formation is suggested (Fig.5), but both of these structures are still a matter of study. [8]

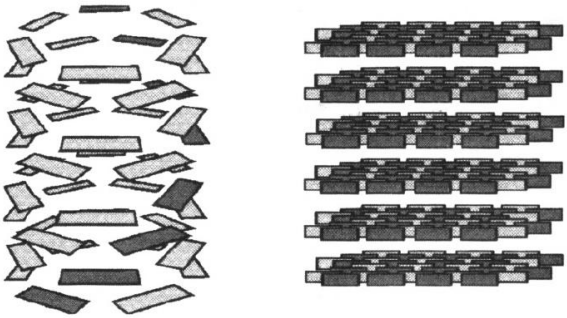


Figure 5. Hollow pipe structure of the CI Acid Red 266 (left) and brickwork structure of a cyanine dye (right) *(Extracted from ref 8)*

4. OBJECTIVES

The main goal of this project is to obtain oriented polymeric nanofibers using nematic phases from chromonic liquid crystals as a template. With that in mind, the work can be divided in several milestones:

- To exchange the dye's original counterion for acrylate, a polymerizable and water soluble one.
- To confirm the liquid crystal formation in water and establish the concentrations at which these are formed.
- To study the structure and thermal stability of the liquid crystals and the optimal polymerization conditions.
- To perform the templated polymerization.
- To characterize the materials obtained in order to prove the formation of nanofibers.

5. EXPERIMENTAL SECTION

5.1. REAGENTS

The dyes and reagents used for this project are summarized on the following table:

Reagent	Supplier	Purity
3,3'-Diethylthiadicarbocyanine Iodide (TdCC)	Alfa-Aesar	≥99%
3,3'-Diethylthiacarbocyanine Iodide (TCC)	Alfa-Aesar	≥99%
Pinacyanol Chloride	TCI	≥93%
Neutral Red — Practical Grade	Sigma-Aldrich	≈60%
Neutral Red — Higher Purity	Sigma-Aldrich	≥90%
Silver Acetate	Sigma-Aldrich	≥99%
Silver Acrylate	ABCR	≥95%

Table 1. Products used in this work

5.2. COUNTERION EXCHANGE

5.2.1. Preparation of 3,3'-Diethylthiadicarbocyanine Acrylate (TdCC)

TdCC acrylate (Fig.6) was prepared by dissolving 120 mg (0.24 mmol) of 3,3'-Diethylthiacarbocyanine Iodide in 30 ml of MeOH. Silver Acrylate was added (43 mg, 0.24mmol) and the reaction mixture (kept in a sealed vial) was stirred in the dark for 48-72h. The mixture was then centrifuged at 4000rpm for 10min and filtered. The remaining solid was resuspended in 5 ml of MeOH and centrifuged under the same conditions, the resulting supernatants were combined and evaporated to dryness under nitrogen flow.

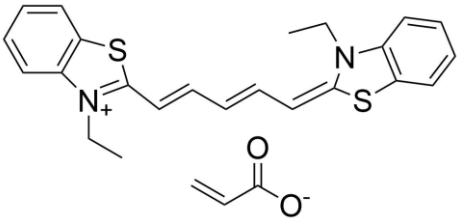


Figure 6. TdCC acrylate

5.2.2. Preparation of 3,3'-Diethylthiacarbocyanine Acrylate (TCC)

TCC acrylate (Fig.7) was prepared following the same procedure as on 5.2.1.

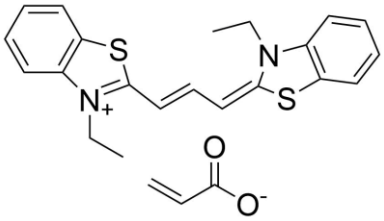


Figure 7. TCC acrylate

5.2.3 Preparation of Neutral Red Acetate/Acrylate

Neutral Red dye was initially purified by adding water, mixing and followed by centrifugation (5000 rpm, three times), the supernatant was recovered and dried. To proceed with the counterion exchange 100 mg of the purified dye was dissolved in 20ml of ethanol with an excess of 10% of silver acetate (or silver acrylate) and maintained under agitation for 24h. After precipitation of the silver chloride the mixture is centrifuged and filtered. The final Neutral Red acetate (or acrylate) (Fig.8) was then obtained by drying under nitrogen flow.

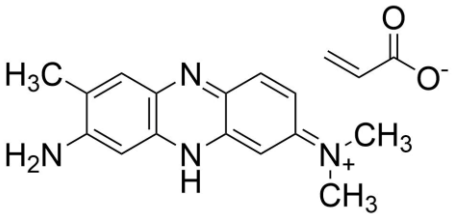


Figure 8. Neutral Red Acrylate

5.2.4. Preparation of Pinacyanol Acetate/Acrylate (PiA)

PiA was initially purified by dissolving Pinacyanol Chloride in water and recovering the insoluble part by filtration (repeated three times before drying).

Once purified, relative molar quantities of 1,1 silver acetate or silver acrylate with 1 of the purified dye were dissolved in ethanol. The mixture was stirred in the dark for 48-72h, and finally filtered and dried under nitrogen flow to yield PiA (Fig.9).

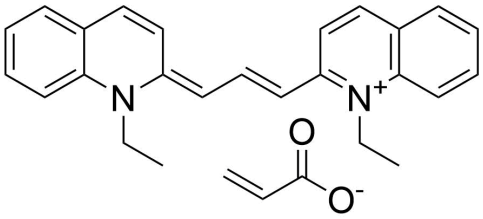


Figure 9. Pinacyanol acrylate

5.3. CHARACTERIZATION

5.3.1. Polarized Optical Microscopy (POM) – Liquid crystal formation and stability

The equipment used was a BX51TRF-6 optical microscope from Olympus, coupled to a digital camera Olympus DP73 connected to a computer.

First of all a qualitative study was performed using POM to determine if the corresponding dye formed liquid crystal phases in water solution.

With this objective, a spatula tip of the compound is put on a microscope slide and covered with a coverslip, to finally add water from a side to see a concentration gradient of the dye in water. Once prepared the sample was observed under polarized light on the optical microscope, if liquid crystal phases were formed we would observe birefringent zones at the interface with water.

POM was also used to confirm the liquid crystal phase formation of solutions of known concentration.

Temperature stability of the synthetized dyes was checked using a hot stage T95-PE from LINKAM Scientific Instruments Ltd.

The sample was put on a microscope slide, covered with a coverslip and sealed with superglue 3. Then it was put on the hot stage of the polarization microscope and heated from room temperature to 65º

5.3.2. SEM – Polymer fibers observation.

SEM observation was performed on samples after polymerization. The equipment used was a TM-1000 Tabletop Electron Microscope from Hitachi. The sample is deposited on a silicon wafer, evaporated, and put on an adhesive carbon slide in order to make it conductive.

Higher resolution SEM was performed with an Hitachi S-3500N at ICM (Institut de Ciències del Mar), in this case, the silicon wafer with the dry sample deposited is first covered with a gold nanolayer of 18 nm (metallization) in order to make it more conductive and improve the images obtained.

5.3.3. Small Angle X-ray Scattering (SAXS)

SAXS analysis were performed on the known concentration samples of each dye before and after polymerization. The sample is introduced in a SAXS glass capillary (Hilgenberg nº 14, outside diameter 1mm) and centrifuged for 3 minutes at 1750rpm in order to make it slide to the capillary end, filling approximately 1/3 of it. The top is cleaned with ethanol and sealed with a blowtorch.

The equipment used was a Hecus S3 Micro SAXS-WAXS coupled to a Kratky camera, 2 PSD 50M Detectors, Cu K alpha 0.1542 nm radiation and a Peltier Temperature controller (-10 to 120 ºC)

5.3.4. Infrared Spectroscopy (IR)

Infrared spectroscopy was performed on samples before and after polymerization, in order to see changes in the bands corresponding to the polymerizable counterion. The equipment used was a Nicolet Avatar 360 FT-IR spectrophotometer, with an Smart ITR Sampling Accessory in the 4000-400 cm^{-1} range.

5.4. POLYMERIZATION

5.4.1. Initial tests

Two different polymerization initiators were tested at two different initiator/monomer ratios. The polymerization was performed in an oil bath at 60 ºC under stirring for 4h, the only reagents were silver acrylate and the corresponding initiator.

Initiatior	**Initiator/monomer ratio** [mol/mol]
2,2'-azobis(2-methylpropionamidine)	0.05
	0.1
Potassium persulfate (KPS)	0.05
	0.1

Table 2. Polymerization tests

In most cases the solutions initially transparent were gradually evolving to a more turbid appearance, sign of the formation of polymer. Polymer presence was confirmed with SEM imaging, the best option found was with KPS as initiator and initiator/monomer ratio = 0.1

5.4.2. Polymerization with liquid crystal phase as template

Initially solutions at a concentration where nematic liquid crystal phase is formed were prepared, starting with a 3% dye concentration by dissolving 30mg in 1 ml of MiliQ water. In all cases, a concentration between 3-5% was needed. The prepared solutions were observed with POM, aiming to see a homogeneous liquid crystal phase formation (as described in 5.3.1).

After confirming the correct concentration, the polymerization was performed in sealed vial. Since the molecular weight of each dye is different, different weights of KPS (initiator) will be needed in each case, on table 3 necessary quantities are described for each dye, a volume of 1ml of the dye solution and the corresponding concentration.

Dye (acrylates)	Concentration (%)	Molecular weight (g/mol)	KPS (mg)
TdCC	4.5	461.57	1.82
TCC	3.5	436.54	2.17
PiA	3.5	424.48	2.23
Neutral Red	-	-	-

Table 3 . Polymerization conditions

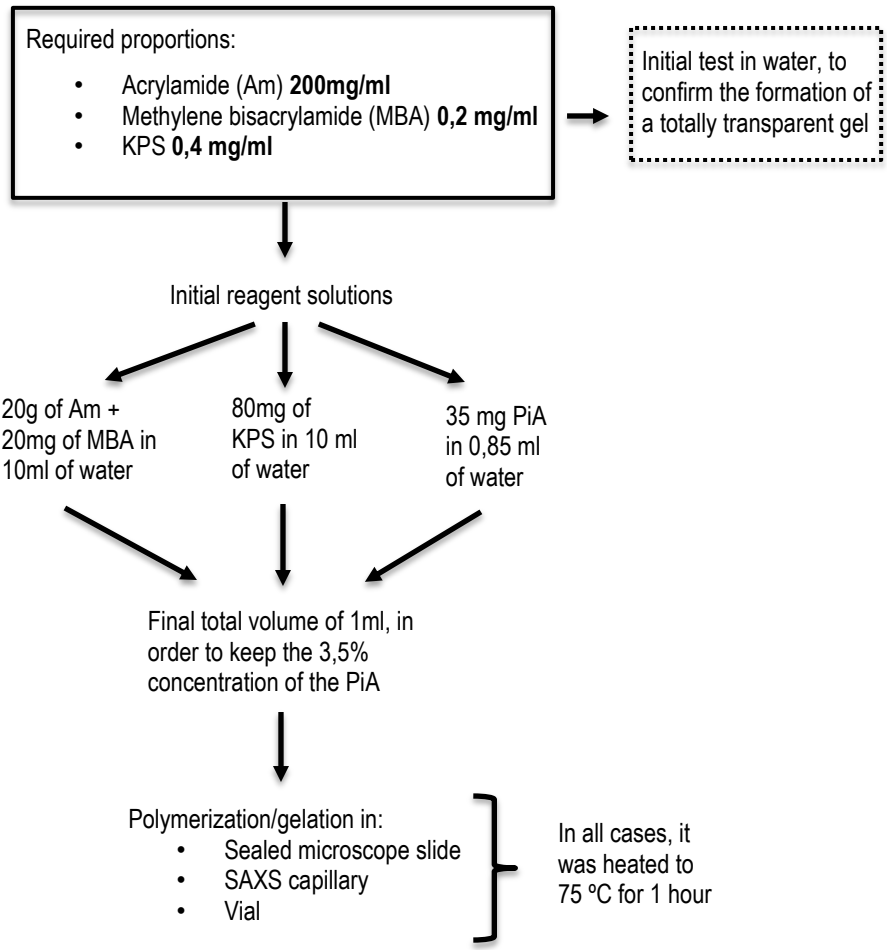
Since the quantities needed are very small, a more concentrated solution of initiator is initially prepared and 0.1 ml of the solution containing the initiator is added, as an example, in the case of PiA:

22.3 mg KPS → 2ml H_2O, 0.1 ml of this solution → solution containing the PiA

Additionally, a droplet of the prepared solution was put on a microscope slide with a secure-seal imaging spacer of 0.12mm depth, covered with a coverslide and sealed with superglue 3. In both cases it was heated to 60ºC for 20h, in the case of the microscopy slide on a heating plate and for the solution vial on an oil bath with magnetic stirring.

5.4.3. Hydrogel preparation

An acrylamide hydrogel containing PiA was prepared as explained in the following scheme:



Scheme 1. Preparation of an acrylamide hydrogel with PiA

At the same time the gelation occurs, polymerization will also take place with the PiA as template.

6. RESULTS AND DISCUSSION

6.1 COUNTERION EXCHANGE

The corresponding acrylate of each of the dyes was first of all observed with the qualitative technique described on section 5.3.1. If the counterion exchange had been successful and liquid crystal phases were formed, we would observe birefringent zones at the interface with water, as we can see in Fig.10. In contrast, if the counterion exchange is not successful, the dissolution and formation of liquid crystal phases will not be possible since the dyes used are not soluble in water with their initial counterion (chloride or iodide), the acrylate increases the water solubility of the compounds.

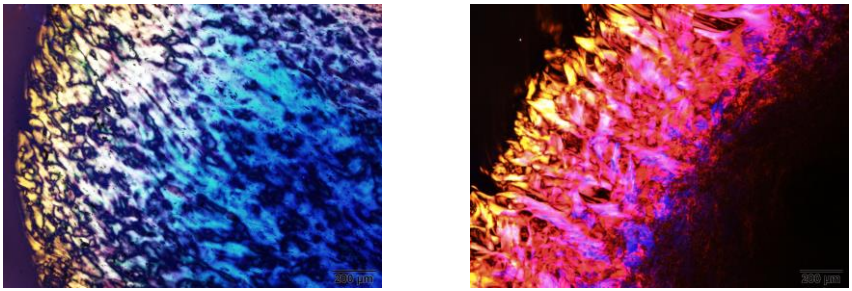


Figure 10. TdCC acrylate (left), Pinacyanol Acrylate (right). The water phase is on the far left side of each pictue

The optical textures seen on figure 10 are characteristic of the chromonic phases, an evolution can be seen from a diluted N phase to a more concentrated M phase as the distance from the water phase increases. There is a wide range of optical textures that can be formed, in figure 10 we can see as an example the “tiger-skin” texture of the N phase of TdCC.

This test was performed on all four of the prepared dyes, resulting on liquid crystal formation in all of them excepting Neutral Red, probably because the original dye used was less pure

(about 60%) than the other three used (90-99%). An additional test was later performed with a higher purity neutral red, it was repeated three times with the same conditions but only in one case the synthesis was successful (Figure 11), since it does not seem to be a reproducible result this dye was not used for further studies on this work.

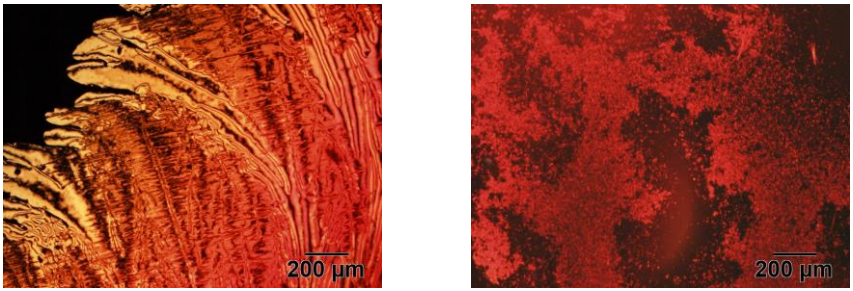


Figure 11. Neutral red after succesful counterion exchange (left), Neutral red after failed counterion exchange (right)

6.2 POLYMERIZATION

6.2.1. Known concentration samples

Once confirmed the liquid crystal formation, solutions of concentration where nematic liquid crystal phases are formed were prepared, to confirm the formation of homogeneous nematic phases the samples were observed with POM (Fig.12).

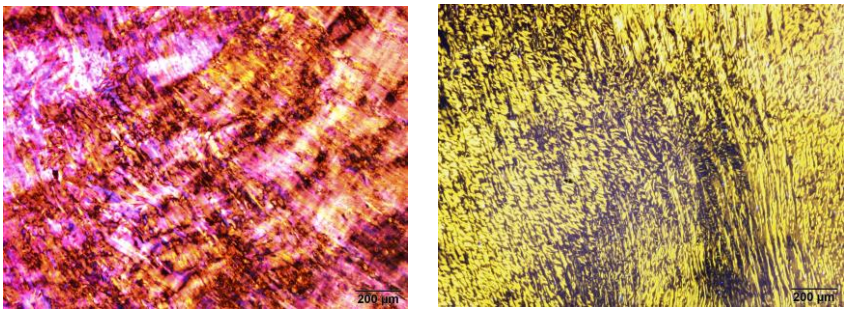


Figure 12. 3.5% PiA solution (left), 4.5% TdCC solution (right)

In the case of TdCC a concentration of 4,5% was needed, for PiA and TCC it was 3,5%.

6.2.2. Thermal stability

Since polymerization was going to be performed at 60ºC, it was necessary to check the thermal stability of the sample on this range, in Fig.13 we can observe optical textures of TdCC at room temperature and at 65ºC

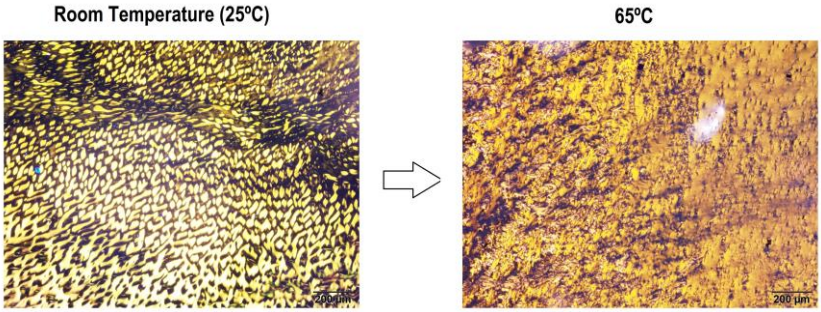


Figure 13. Thermal stability test of TdCC

It could be seen that the increase of temperature does not affect the liquid crystal formation, so the polymerization could be performed at this temperature without risking to lose the chromonic phases.

6.2.3. Characterization

After performing the polymerization as described in section 5.3.2, the solutions before and after polymerization were characterized with SEM imaging, IR spectroscopy, SAXS and optical microscopy.

Small Angle X-ray Scattering (SAXS)

First of all, a SAXS study of the samples before and after polymerization was performed (Fig.14) in order to confirm the initial LC formation and that this structure remains all along the process, since if the structure is lost during the polymerization it would not be possible to use these mesophases as template for the polymerization.

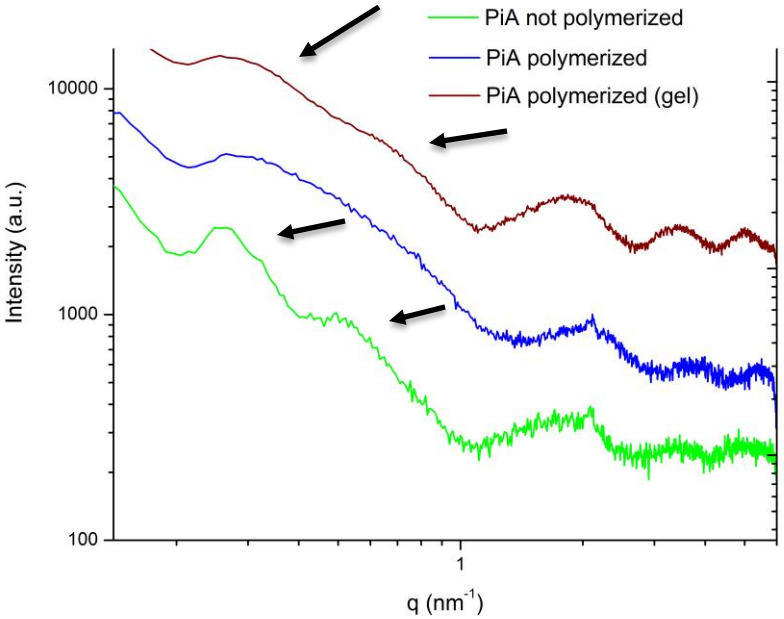


Figure 14. PiA SAXS analysis

Comparing the SAXS curves (Fig.14) before (green) and after polymerization (blue) it can be seen that structures are present all along the process, although some changes are observed. The presence of multiple maxima and minima are a fringerprint of aggregates with low polidispersity in their characteristic lengths. The positions of those maxima and minima remain almost constant before and after polymerization.

In order to compare to an amorphous non-structured sample, SAXS curve of Mili-Q water used in the synthesis is shown in Fig.15:

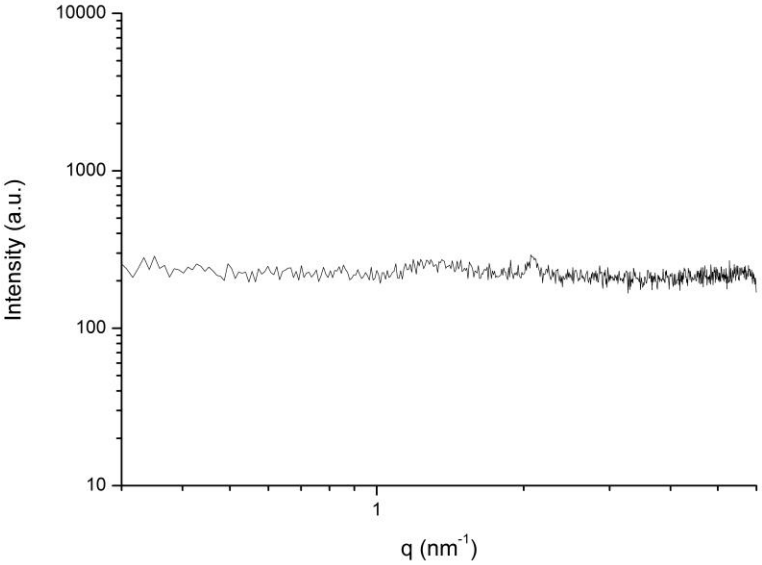


Figure 15. SAXS curve of MiliQ water

The SAXS curve for Mili-Q water seen in Fig.15 does not show any peaks or maxima as expected for an amorphous, non-structured sample.

Regarding the other two dyes, similar results indicating liquid crystal phases were obtained and their SAXS curves can be seen in Appendix 2.

The SAXS curve for the PiA has been further analysed in order to obtain more information about the self-assembly of this dye. Comparing the obtained SAXS curve with the one from Ref.13 (Fig.16) it can be seen that the minima and maxima of the curves are in almost the same position, implying that a model similar to the one suggested in Ref.13 could be applied for the PiA sample.

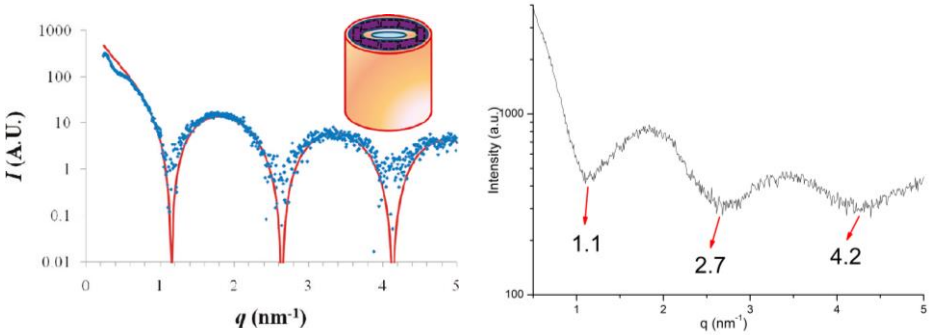


Figure 16. Comparison between obtained curve for PiA (right) and curve from Ref.13 (left)

The model used to fit the curve was the one corresponding to monodisperse infinitely long tubes with three layers in their walls (inner and outer layer containing the counterions). In Ref.13 the parameters estimated from curve fitting are a tube diameter of 4.6nm for a fixed wall thickness of 0.3nm (corresponding to the size of a benzene ring). Taking in account that the pinacyanol molecular length is about 1.7 nm, this implies that each stacked ring would consist of around 8 molecules.

The resulting structure from this information is a hollow-pipe model similar to the one showed in Fig.5.

Infrared Spectroscopy (IR)

In the polymerization of acrylate a double bond transforms into a single bond, and that change should be visible comparing IR spectra before and after polymerization, for comparison spectrum of silver acrylate alone was also performed (Fig.16).

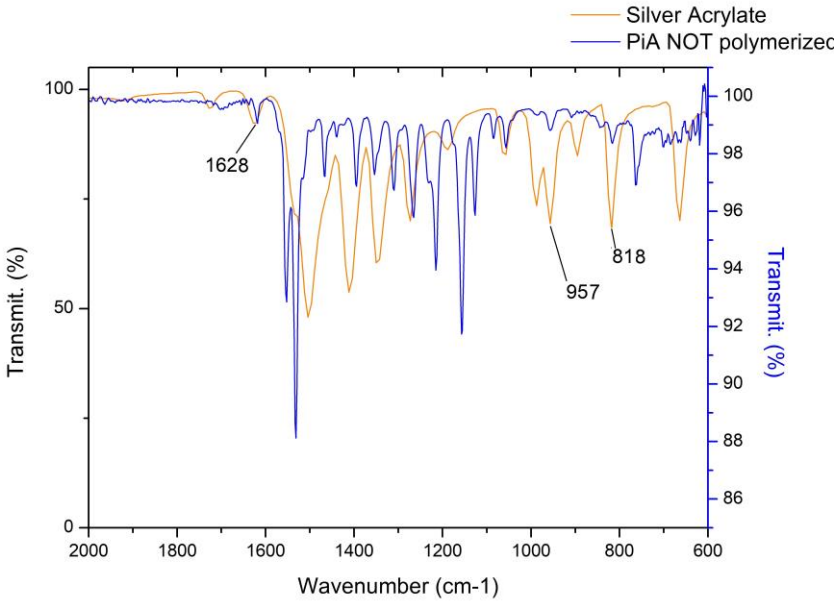


Figure 17. Spectra comparison of PiA with Silver Acrylate alone.

The three bands that are labelled on the spectrum are the ones that correspond to the silver acrylate and also appear on the PiA one. It can be seen that there are a lot of bands in common between 1000 and 1600 cm^{-1}, but these ones cannot be really considered for our study since in this zone the Pinacyanol alone has a lot of bands, in table 4 we can see a correlation between these bands and the silver acrylate bands that also appear in this zone

Wavenumber (cm^{-1})	
Silver Acrylate	**Pinacyanol Chloride**
1188	1157
1273	1265
1350	1354
1412	1466
1504	1531
1628	1618

Table 4. Comparison between silver acrylate and pinacyanol chloride

To really being able to consider the bands from figure 16, it was necessary to assign them to its corresponding bond from the silver acrylate. It was possible to relate these bands to the double bond, as we can see in table 5, even if the band in 1628 cm^{-1} could be masked by the Pinacyanol band, it will still be checked because it corresponds to a C=C st.

Obtained wavenumber (cm^{-1})	Reference[9] wavenumber (cm^{-1})	Band Assignment
818	810	=CH δ oop
957	960	=CH δ oop
1628	1635	C=C st.

Table 5. Assigned bands from the acrylate spectrum, compared for a C=C-C=O molecule.

So these three bands were the reference used to confirm the polymerization, as we can see in Fig.17:

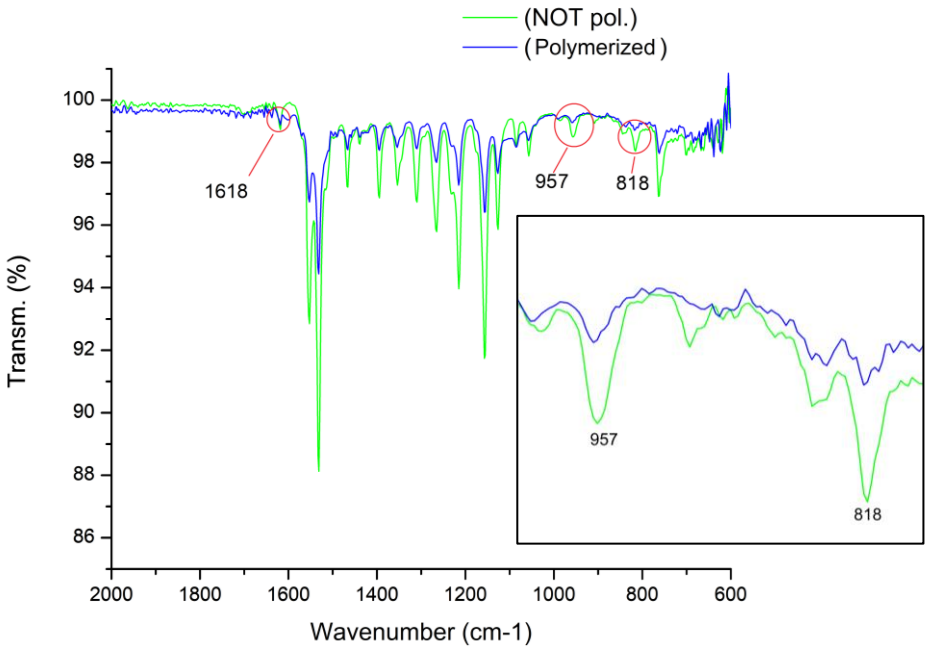


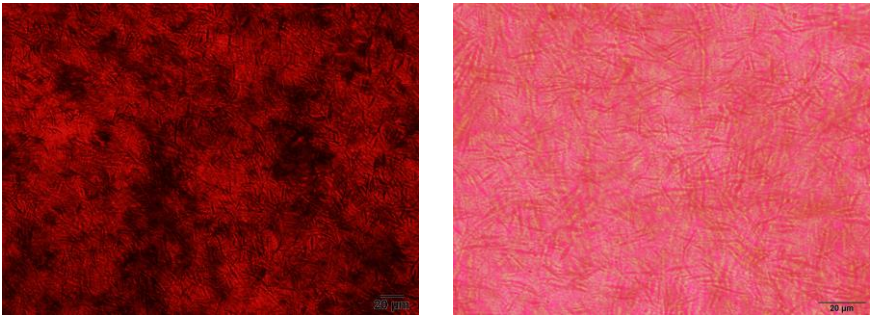
Figure 18. PiA IR spectra before and after polymerization

It can be seen that the reference bands (circled in red) nearly disappear after polymerization, it is true that a general decrease of intensity is observed in all bands, but in the reference bands it is a more noticeable decrease. The band at 1618 cm^{-1} it does not disappear completely because as it has been said before it may be overlapped with the C=C st. of the pinacyanol molecule.

For the other two dyes (TdCC and TCC), the IR study does not give that much information as a representative change in band intensity cannot be seen, their corresponding spectra can be seen in Appendix 1.

Optical Microscopy: Bright field and POM

Optical miscroscopy was used in order to confirm the formation of liquid crystal phases even after polymerization. In the case of TCC, the sample polymerized directly in the microscope slide is analyzed, as we can see in Fig.18 there is homogeneous formation of needle-like



structures.

Figure 19. POM (left) and bright field (right) images of TCC polymerized

In the case of PiA, formation of fibrous structures is observed all along the solution, and these still coexist with the initial nematic phase, this can be appreciated in Fig.19 since it is the same zone and magnification with the two different techniques, POM to see the liquid crystal phase and bright field to make sure these structures are not a matrix optical effect.

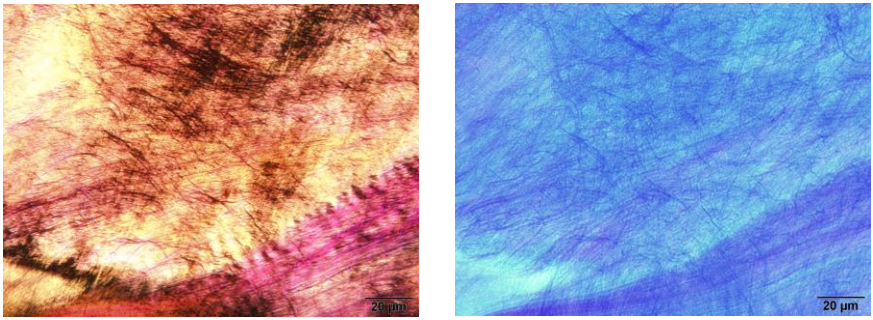


Figure 20. POM (left), bight field (right) of polymerized PiA

In Fig.20 the fibers formed in the PiA solutions can be observed at a higher magnification:

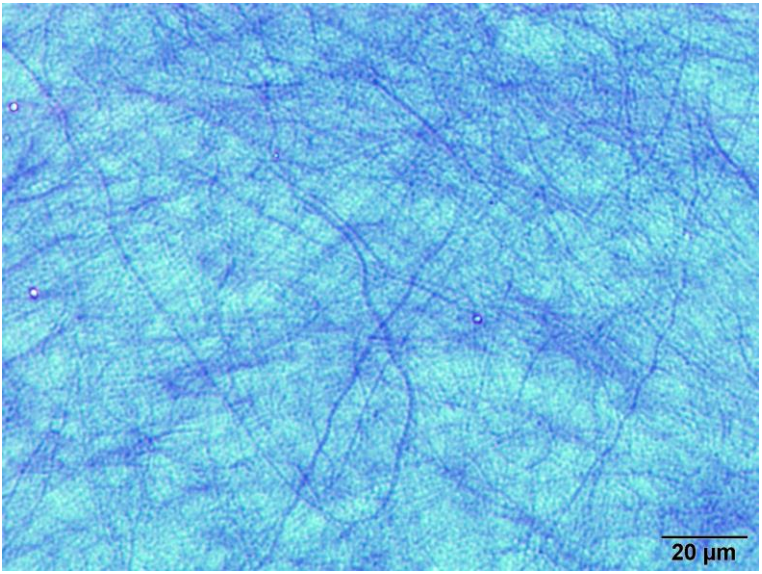


Figure 21. PiA fibers (bright field)

In this case it is clear that some fiber-like material has been formed, there are fibers of approximately 100-500 nm of thickness and a few microns length.

Scanning Electron Microscopy (SEM)

In Fig.20 it can be seen a SEM image of the TdCC polymerized solution, there are some needle-like aggregates of a size between 30-50 μm that could have formed from the acrylate polymer, but these could also be only crystallized reactants.

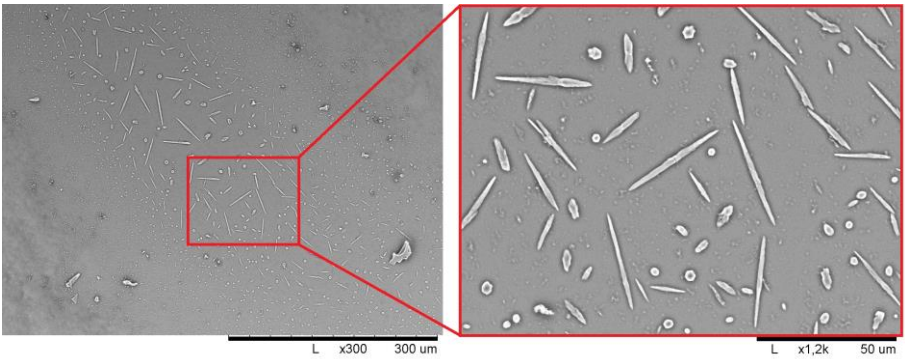


Figure 22. SEM images of TdCC polymerized solution

In the case of TCC (Fig.21), formation of needle-like structures or aggregates can also be observed, and these cannot be seen at all in the non-polymerized sample.

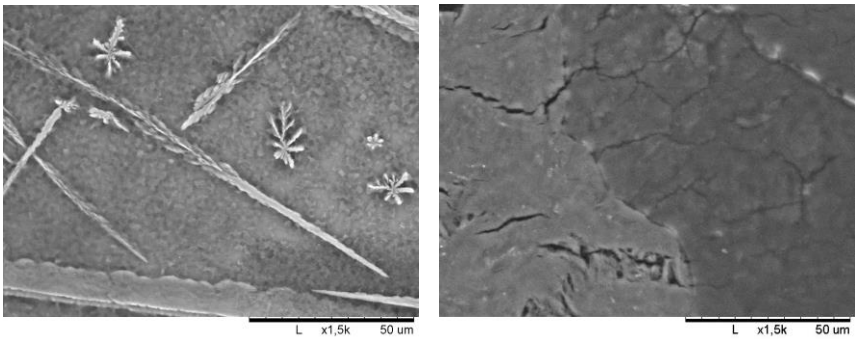


Figure 23. TCC polymerized (left) and non-polymerized (right)

These structures were already observed in figures 19 and 20 through optical microscopy, and as it has been said they are probably not originated from a liquid crystal templating, are more likely to be formed from crystallization from some of the reactants.

Having a closer look on a more diluted solution of the TCC dye (Fig.22) one can observe the presence of some small fibrous material that could be more related to the polymerization templated by the liquid crystal phases:

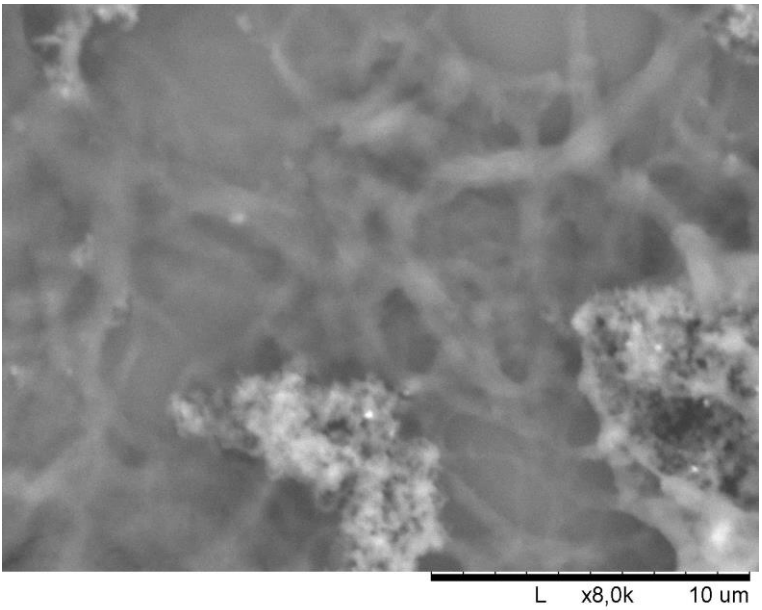


Figure 24. Fibers from the TCC sample

The material seen on the surface of the fibers in figure 22 is probably an excess of some of the reactants, as it is totally amorphous. The fibrous structures are approximately between 100 and 500 nm wide, and it looks like they're interconnected. Considering that the columns or pipes formed in the liquid crystal phases are some orders of magnitude smaller, these fibers are probably formed by several columns, a TEM study could be performed to determine their internal structure.

In the case of PiA the most encouraging results of all three dyes are obtained (Fig.23), since a more defined and continuous fibrous structure can be observed:

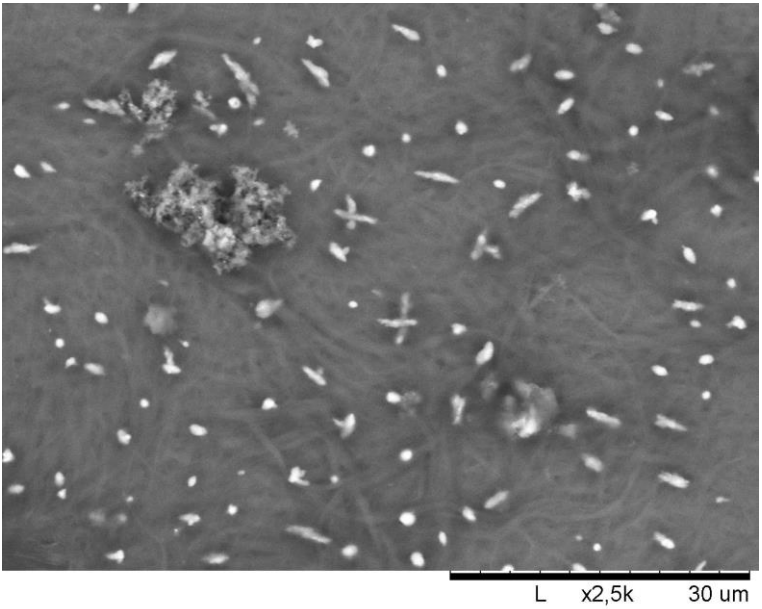


Figure 25. PiA acrylate polymer fibers

The polymer fibers on the background of Fig.23 are less than a micron wide, and a few microns in length, as it was already suggested with optical microscopy observation. The material on the surface might be an excess of some of the reactants that was not properly washed off.

To verify that these fibers are originated in the polymerization, a sample of the solution before polymerization is observed, in Fig.24 a picture of the non-polymerized sample is compared to a picture of a polymerized sample displaying fibers.

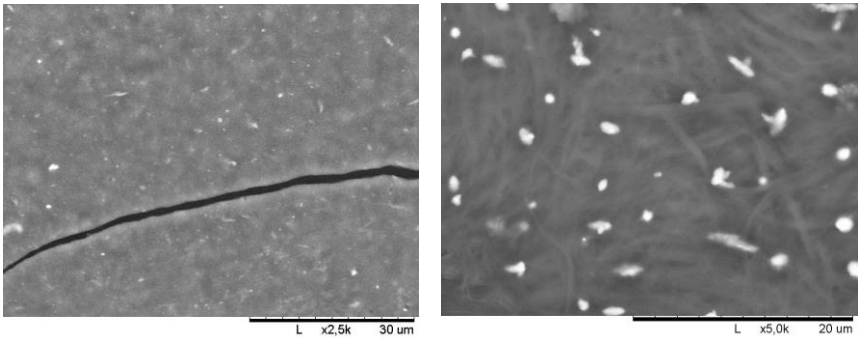


Figure 26. Comparison between before (left) and after polymerization (right)

A study with a higher resolution SEM equipment was done on the same sample shown in figures 23 and 24 in order to have more information about those fibers, the resulting images can be seen in Fig.25 and 26.

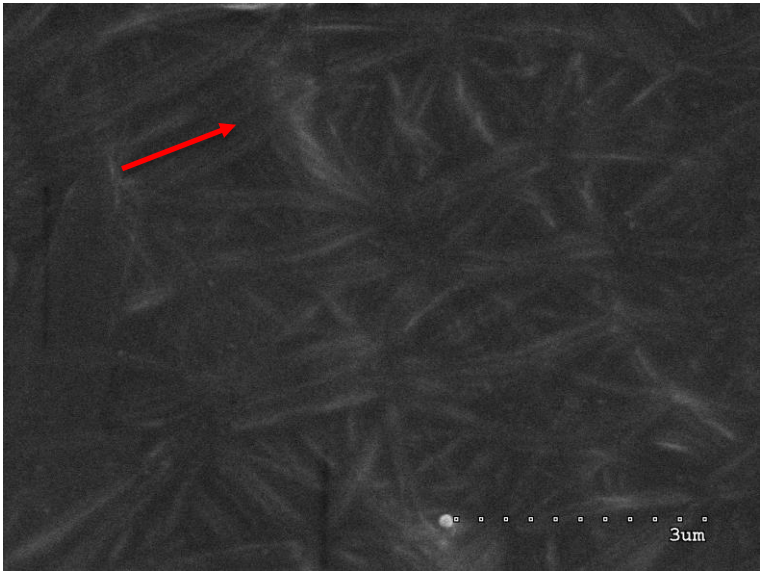


Figure 27. High resolution image of PiA polymerized sample

The observed fibers are between 100 and 300 nm wide, their length is hard to determine since they are very interconnected. It seems that they are formed by various thinner threads combined, and having a look at the fiber marked with a red arrow (Fig. 25) reveals that the fibers can also twist.

It is also remarkable that it looks like there are nodes where the fibers connect, these are more clearly seen in Fig.26 (marked with a red arrow)

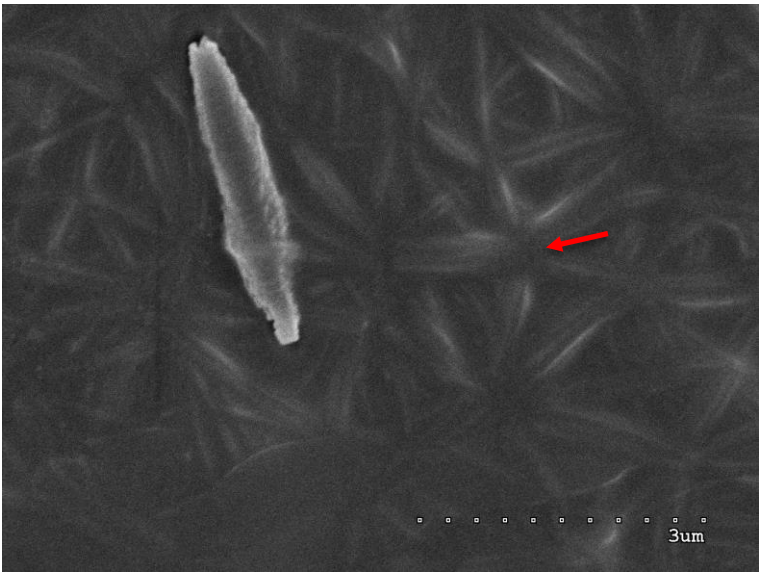


Figure 28. Fiber nodes

10. CONCLUSIONS

Counterion exchange has been successfully performed on three of the four used dyes (TdCC, TCC and PiA), with the newly added acrylate counterion the dye molecules became soluble in water and liquid crystal formation was possible. It has been studied the concentration at which stable nematic liquid crystal phases are formed, in all cases it was between 3,5 and 5%. Since the main objective of the work was to perform a polymerization at higher temperatures, their thermal stability was also studied, confirming liquid crystal formation in the polymerization temperature range.

Liquid crystal nematic phases have been used as a template for the synthesis of polymeric nanofibers, fibers of a few microns length and about 100-500 nm of thickness were obtained in the case of PiA. For the other two dyes only in TCC it could be confirmed some possible polymeric structure formation. The polymerization was initially verified through IR spectroscopy, and the final material was characterized with SEM, SAXS and POM. SAXS confirmed the structural stability of the liquid crystal mesophase before and after polymerization. In PiA it could also be appreciated through POM that after polymerization the nanofibers still coexist with the liquid crystal phase, suggesting a successful templating.

This kind of templating with liquid crystals was only previously successfully tested with silica nanofibers, the use of polymerizable organic counterions like acrylate opens a wide range of possibilities, in further studies other dyes and other organic counterions could be tested.

11. REFERENCES AND NOTES

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12. ACRONYMS

LC: Liquid Crystal

CLC: Chromonic Liquid Crystal

TCC: 3,3'-Diethylthiacarbocyanine

TdCC: 3,3'-Diethylthiadicarbocyanine

PiA: Pinacyanol Acrylate

SAXS: Small Angle X-Ray Scattering

IR: Infrared

POM: Polarized Optical Microscopy

SEM: Scanning Electron Microscopy

APPENDICES

APPENDIX 1: IR SPECTRA OF TDCC AND TCC

3,3'-Diethylthiadicarbocyanine Acrylate (TdCC)

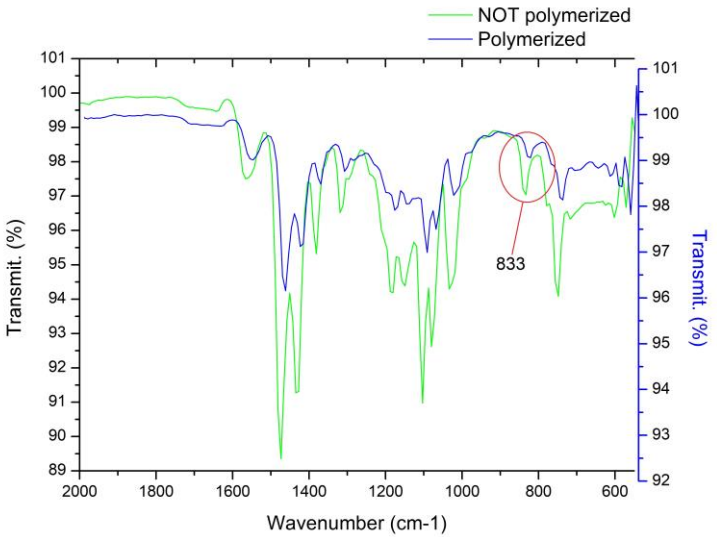

Figure 27. IR spectrum of TdCC acrylate before and after polymerization

Changes in intensity are appreciated, but these are all along the spectrum, so it is difficult in this case to correlate the intensity variation with the polymerization, only the band at 833 cm^{-1} could be interpreted this way.

3,3'-Diethylthiacarbocyanine Acrylate (TCC)

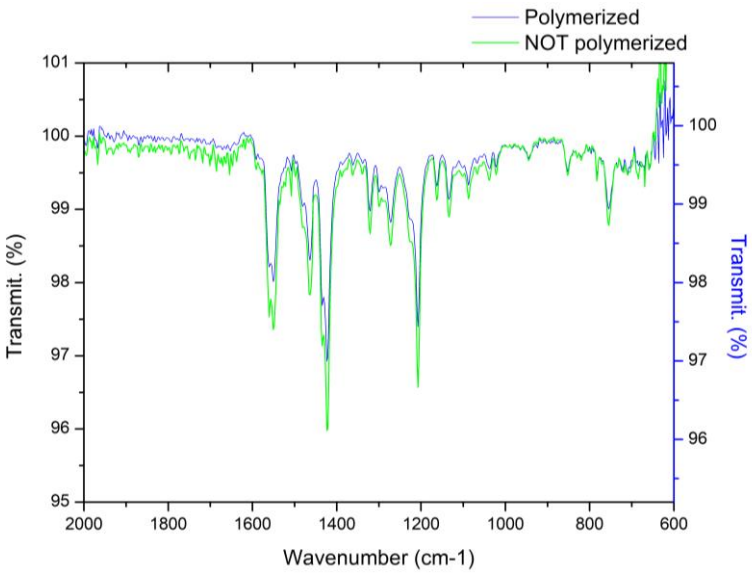

Figure 28. IR spectrum of TCC acrylate before and after polymerization

In this case, changes in intensity cannot be appreciated in the region of interest, it can be because polymerization was not successful or because IR spectroscopy is not the best technique to characterize this molecule.

APPENDIX 2: SAXS CURVES OF TDCC AND TCC

3,3'-Diethylthiadicarbocyanine Acrylate (TdCC) – Before polymerization

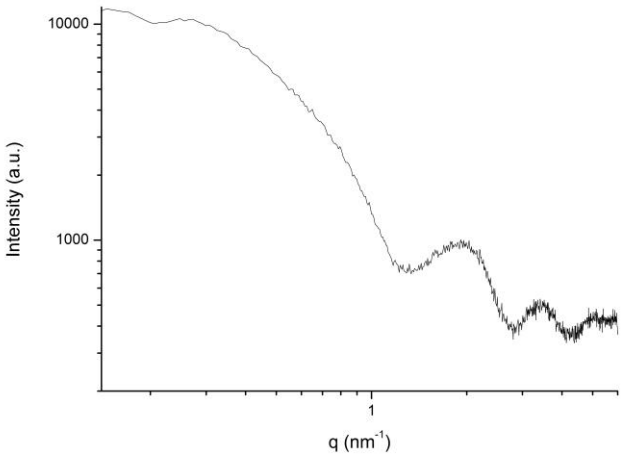

Figure 29. SAXS curve of TdCC acrylate before polymerization

In this case it is possible to see that there is formation of a structured phase (corresponding to a liquid crystal phase) since there is the presence of maxima and minima.

3,3'-Diethylthiacarbocyanine Acrylate (TCC) – After polymerization

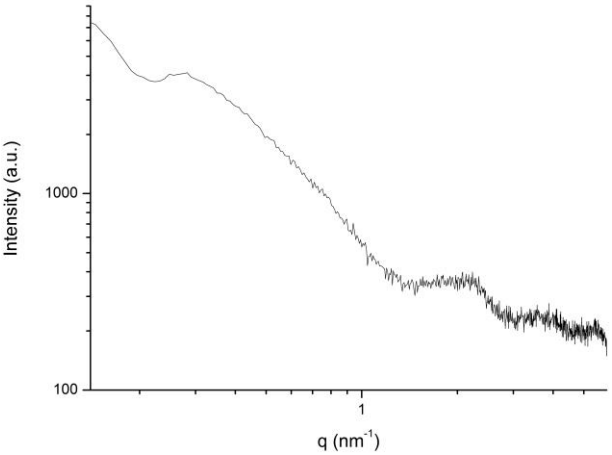

Figure 30. SAXS curve of TCC acrylate after polymerization

In this case it can be also confirmed the structural stability of the liquid crystal, since there is the presence of maxima and minima after polymerization.